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(54) Title: SUBSTRATES WITH IMPROVED OXIDATION RESISTANCE

100

101	SELECT AND WEIGH THE CONSTITUENTS Cu, E, AND OPTIONAL Ni.
102	MELT THE CONSTITUENTS.
103	(OPTION) REMELT TO ENHANCE HOMOGENEITY.
104	SHAPE THE SOLIDIFIED MELT AND HOMOGENIZE BY HEAT TREATMENT.
105	DEFORM THE SHAPE TO A SMALLER SIZE AND RECRYSTALLIZE TO FORM A SMALL GRAIN SIZE IF DESIRED.
106	DEFORM THE SHAPE IN AN AXIALLY SYMMETRIC MANNER TO A SMALLER SIZE.
107	DEFORM THE ALLOY IN A PLANAR MANNER TO A REDUCTION IN THICKNESS EXCEEDING 85% BUT NOT MORE THAN 99.9%
108	HEAT TREAT AT A TEMPERATURE EXCEEDING 250°C BUT NOT MORE THAN 95% OF THE MELTING TEMPERATURE.
109	(OPTION) ANNEAL IN A GAS FLOW WITH LOW OXYGEN, PARTIAL PRESSURE TO FORM AN EPITAXIAL OXIDE LAYER.

(57) Abstract

An alloy article having improved oxidation resistance and biaxially textured surfaces formed by thermo-mechanical techniques. The alloy article has up to 60 atomic % nickel, 0.1 to 25 atomic % of an oxide former selected from Mg, Al, Ti, Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Ho, Lu, Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La, and mixtures thereof, with the balance copper. The surface smoothness of the article may be improved by thermomechanical techniques without impairing its surface texture. The CTE of the article may be reduced and its mechanical strength increased by incorporation of additional materials into the article without impairing its surface texture. The alloy article is used as a conductive substrate for superconducting composites where the substrate is coated with a superconducting oxide. Methods of producing the alloy article by melting and sheath and core techniques are also disclosed.

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## SUBSTRATES WITH IMPROVED OXIDATION RESISTANCE

### Background of the Invention

The present invention relates to substrates for superconductors, and more particularly to copper based and copper-nickel based substrates, which have enhanced oxidation resistance, for the deposition of high temperature superconducting copper oxide layers to form superconducting coated conductors. Applicable superconducting materials include YBCO ( $\text{YBa}_2\text{Cu}_3\text{O}_x$ , or Yttrium-Barium-Copper-Oxide) and  $\text{REBa}_2\text{Cu}_3\text{O}_x$ , in which the Y component of YBCO has been partially or completely replaced by rare earth (RE) elements. Other superconducting phases of these yttrium and rare earth superconductors, and other superconducting copper oxides of the bismuth, thallium, and mercury families can also be used.

YBCO ( $\text{YBa}_2\text{Cu}_3\text{O}_x$ ) is an important superconducting material for the development of superconducting tapes that can be used in superconducting transmission cables, superconducting current leads, superconducting magnets for transformers, superconducting magnets for AC and DC motor applications, and current limiters, as well as other electrical conductors. These applications are based on a basic property of a superconducting material: it has no electrical resistance when cooled below its transition temperature, and can carry an electric current without power dissipation.

In the production of superconducting coated conductors, thin substrate tapes (or foils) are typically coated with a thin buffer layer, which in turn is coated with a superconducting layer. A suitable heat treatment is then performed to optimize the superconducting properties of the superconducting layer. One of the functions of the substrate is to impart mechanical strength to the resulting superconducting tape. A second function, which depends on the process type, is to act as a template for a well-textured buffer layer. Compared to

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the substrate material, this buffer layer provides a much better deposition surface for the superconductor layer in terms of lattice match, texture, coefficient of thermal expansion (CTE) and chemical compatibility. To obtain

5 good superconducting properties, the buffer layer is preferably biaxially textured. In the particular case of a cubic or tetragonal buffer layer material, the lattice of the buffer layer is oriented such that the cube face is parallel to the tape surface. In addition, the cube

10 edge in each crystallite is parallel to the cube edge in all neighboring crystallites.

Some specialized techniques such as Ion Beam Assisted Deposition (IBAD) or Inclined Substrate Deposition (ISD) can deposit a biaxially textured buffer

15 layer on top of a random polycrystalline or even amorphous substrate. In general, these deposition techniques are very slow or are effective in only a narrow region, and they are not suited for large scale

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and economical manufacturing of superconducting coated

20 conductors. A more advantageous deposition method is the epitaxial deposition of a biaxially textured buffer layer (or YBCO superconducting layer) on top of a biaxially textured metallic substrate. Examples of epitaxial growth by vapor deposition, electroplating, or oxidation,

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25 ~~in which native oxide layers grow on parent metals, are~~ numerous and well known, as is the fact that many metals can form biaxial textures. Some of these biaxial textures in metals are quite useful for deposition of buffer layers and YBCO superconducting layers. For

30 example, a biaxial texture can be obtained in many rolled, face-centered cubic (fcc) metals, which when properly rolled and heat treated, result in a well-developed, and very useful, texture. The cube faces are parallel to the rolled surface and a cube edge typically

35 points in the same direction as the rolling direction.

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Such a texture is called a cube-on-cube texture, with a crystallographic notation of (100)[001]. A second well known cube texture is the Goss texture (100)[011].

Another well-known biaxial texture is the annealed brass texture, often indicated by (113)[211]. These textures, and many other biaxial textures, are also referred to as sheet textures. In the following description of the invention the (100)[001] texture will be referred to as the "cube" texture.

One method to obtain a biaxially textured buffer layer is to deposit the buffer layer epitaxially on a biaxially textured substrate. In this method, the substrate material needs to meet certain requirements. The substrate must have a lattice constant and a coefficient of thermal expansion (CTE) which are compatible with the buffer layer material and also with the superconducting layer. Ideally, the substrate will yield a biaxial texture by simple thermo-mechanical means. The substrates are preferably non-magnetic and are electrically conductive at cryogenic temperatures, that is, at temperatures between room temperature and that of liquid helium, which is 4.2 degrees Kelvin. The substrate must also be relatively strong at room temperature, and oxidation resistant at elevated temperatures. There are several metals, such as copper or nickel, that can be biaxially textured by rolling a selected copper or nickel stock, followed by a suitable heat treatment. However, these pure metals have significant drawbacks in that they are either ferromagnetic (Ni) or are easy to oxidize (Cu). These properties are detrimental to the superconducting properties of an oxide layer and to the deposition of buffer layers on the substrate.

Generally speaking, alloys are much more difficult to biaxially texture than pure metals. It is known that

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some binary alloys (a single phase mixture of two metals) can be made into a biaxially textured tape. One example of a cube texture, which has been produced in an alloy, is iron-nickel, but this alloy has proven to be  
5 ferromagnetic. In addition, binary copper-nickel alloys with small quantities of nickel have previously been textured, however those working in the field believed that the maximum Ni content in the Cu-Ni alloy should not exceed 4.2 % nickel.

10 Non-ferromagnetic and oxidation resistant biaxially textured alloys which are useful as substrate materials for superconductors, have not been readily available.

#### Summary of the Invention

15 The present invention features biaxially textured alloy articles having biaxially textured surfaces and improved oxidation resistance. The alloys can have the composition of  $\text{Cu}_{100-x-y}\text{Ni}_x\text{E}_y$ , where the Ni content  $x$  can vary, and the concentration  $y$  of the oxide former E can  
20 vary between 0.1 and 25 atomic %, with the balance,  $100-x-y$ , atomic % being copper. Preferably,  $x$  is from about 0 to about 45 atomic percent, more preferably from about 0 to about 48 atomic percent, and most preferably from about 0 to about 50 atomic percent. When the magnetic  
25 properties of the alloy are less important,  $x$  can be up to 60 atomic percent.

The alloy articles of the present invention can be for use as substrate materials for superconducting copper oxide coatings, the combination forming a superconducting  
30 copper oxide coated conductor. For use in YBCO or REBCO coated conductors, for example, the oxidation resistance of the substrate material needs to be as high as possible. The alloys can be processed by thermomechanical methods to form biaxially textured substrates. Oxide  
35 formers, which form stable oxides, are included in the



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alloy to enhance its oxidation resistance during various heat treatments. In most instances, the resulting surface texture is a cube texture with no substantial secondary texture. These alloy articles are non-ferromagnetic and form good substrate materials for subsequent epitaxial buffer layer and superconductor layer deposition, for use in a variety of products.

The present invention provides for binary, ternary, or quaternary alloy articles by the inclusion of one or more additional oxide formers which can improve the oxidation resistance of the alloy articles over copper or copper-nickel alloys. This invention uses the protective scale forming abilities of oxide former and incorporates this capability into the substrate production method. In certain aspects of the invention, the properties of the alloy articles may be further enhanced, without impairment of its biaxial surface texture, by the inclusion of dispersed oxide particles, which strengthen the alloy, or CTE-reducing materials which tailor its CTE to its intended purpose.

There are several principles of importance in selecting an oxide former and in some instances, combinations of several oxide formers may be used. The chosen oxide former must oxidize easily and form stable oxides. In order to be effective, the oxides  $EO_2$  (E representing the oxide former) should be more stable, both kinetically and thermodynamically, i.e. have higher absolute energies of formation, than Cu or Ni oxides. Examples of oxide formers with such stable oxides  $EO_2$  are aluminum (Al), magnesium (Mg), titanium (Ti), zirconium (Zr), hafnium (Hf), yttrium (Y), chromium (Cr), gallium (Ga), germanium (Ge), beryllium (Be), silicon (Si) and the rare earth elements lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), Samarium (Sm), europium (Eu), gadolinium (Gd), terbium, (Tb), dysprosium

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(Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu) and thorium (Th).

The oxide former must also be able to diffuse to the surface of the substrate to form a protective scale, a form of oxidation which is known as external oxidation. The thickness of the protective oxide scale is less than one micrometer, and preferably less than 0.2 micrometer, since and the substrates are quite thin, (25 to 50 micrometers). The protective oxide scale prevents or slows down oxygen diffusion into the substrate during the buffer layer and/or superconducting layer deposition process. Additionally, if some oxygen diffuses into the interior of the substrate, it should bind to the oxide former and form small oxide particles, a process that is known as internal oxidation. Both types of oxidation of oxide formers are beneficial to the substrate, but in accordance with the invention, a thin, highly adherent, stable oxide scale with low oxygen permeability is needed.

The selected oxide former should not induce a random orientation in the substrate, an undesired type of texture, or a mixture of textures in which the undesired textures exceed about 15 %. Desirable textures include, among others, the cube texture, the annealed brass texture, and the Goss texture. Typically, the cube texture is preferred. Most oxide formers which form stable, non-spalling oxide scales, are known to preserve the cube texture in pure Cu only when present in relatively small quantities, typically less than 1.0 to 3 atomic %. The absolute maximum level depends on the nature of oxide former. In accordance with the invention, a similar effect is observed in for homogeneous CuNi alloys.

In accordance with another embodiment of the invention, those alloys with higher percentages of a

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second oxide former are found to be quite beneficial when used as a core material in a substrate or alloy article, in combination with a sheath consisting essentially of Cu, Ni, or CuNi and 0 to 3 atomic % of a first oxide former. The core comprises 0 to 100 atomic % of a second oxide former and nickel with the balance being copper. Preferably, the alloy includes from about 0 to about 45 atomic percent nickel, more preferably from about 0 to about 48 atomic percent nickel, and most preferably from about 0 to about 50 atomic percent nickel. When the magnetic properties of the alloy are less important, the nickel content of the alloy can be up to 60 atomic percent. In a preferred embodiment the second oxide former is included in an amount of 3 to 25 atomic % and in another preferred embodiment the second oxide former is Al, Hf, Yb, Ce, Ti, Zr, or a mixture of these and forms 100 atomic % of the core. Because of the low concentration of the first oxide former in the sheath, the surface of the substrate can be biaxially textured.

20 The core thus provides the added second oxide former, which diffuses towards the external surface of the sheath and forms a protective oxide layer without affecting the biaxial texture, preferably a cube texture, in the surface of the substrate or in any deposited buffer layer or superconducting layer. The core also acts as a site for oxygen adsorption during the various heat treatments, or acts to repair damaged oxide sheathing by providing essential elements. The overall composition of the substrate is 0.1 to 25 atomic % of the oxide former and nickel, with the balance being copper. Preferably, the alloy includes from about 0 to about 45 atomic percent nickel, more preferably from about 0 to about 48 atomic percent nickel, and most preferably from about 0 to about 50 atomic percent nickel. When the magnetic properties of the alloy are less important, the nickel content of

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the alloy can be up to 60 atomic percent. The first and second oxide formers may be the same or different.

In another aspect, the invention features an article that includes an alloy containing copper, nickel  
5 and at least about one atomic weight percent of an additional metal selected from Mg, Al, Ti, Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu, Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La or combinations thereof. The article has a biaxially textured surface, such as a cube  
10 textured surface. The article can be a superconductor substrate. The article can include at least about two atomic weight percent of the additional metal. The article can include at most about four atomic weight percent of the additional metal. The article can include  
15 at least about two weight percent aluminum and/or at most about four weight percent aluminum. The article can include at least about 25 weight percent nickel.

~~Preferably, the article includes from about 0 to about 45~~  
weight percent nickel, more preferably from about 0 to  
20 about 48 weight percent nickel, and most preferably from about 0 to about 50 weight percent nickel. When the magnetic properties of the article are less important, the nickel content of the article can be up to about 60 weight percent.

~~25 In another aspect, the invention features an~~  
article that includes an alloy containing copper, nickel and aluminum. The alloy can further include an additional metal selected from Mg, Al, Ti, Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu, Th, Er, Tm,  
30 Be, Ce, Nd, Sm, Yb, La or combinations thereof. The article has a native oxide exterior formed of alumina. The surface of the article can be biaxially textured, such as cubic textured. The article can be a superconductor substrate.

35 In another aspect, the invention features an

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article including an alloy of copper and at least about 25 weight percent nickel. The article has a biaxially textured surface, such as a cubic textured surface. Preferably, the alloy includes from about 0 to about 45 atomic percent nickel, more preferably from about 0 to about 48 atomic percent nickel, and most preferably from about 0 to about 50 atomic percent nickel. When the magnetic properties of the alloy are less important, the nickel content of the alloy can be up to 60 atomic percent. The alloy can also include at least about one weight percent of Mg, Al, Ti, Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu, Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La or a combination thereof.

The present invention also includes several methods for producing substrates with biaxially textured surfaces and superconducting composites and their resulting products. Among these products and methods are the following.

A preferred embodiment which provides a process for forming an alloy or article with a biaxially textured surface by melting, includes creating a mixture of 0.1 to 25 atomic % of an oxide former and nickel with the balance being copper. Preferably, the alloy includes from about 0 to about 45 atomic percent nickel, more preferably from about 0 to about 48 atomic percent nickel, and most preferably from about 0 to about 50 atomic percent nickel. When the magnetic properties of the alloy are less important, the nickel content of the alloy can be up to 60 atomic percent. A cube textured surface may be obtained if less than about 1 atomic % to 3 atomic % of the oxide former is used. The mixture is melted to form a liquid which is solidified to form an alloy. Remelting is optionally performed to enhance homogeneity. The solidified alloy is shaped and homogenized by heat treatment. Deforming the alloy by

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mechanical techniques, followed by a recrystallization procedure, produces a controlled fine grain size. Again deforming the alloy by mechanical techniques and heat treating the deformed alloy produces a biaxial texture in the alloy. The substrate can optionally be annealed in a low oxygen partial pressure atmosphere to form an epitaxial oxide layer.

Another preferred embodiment of the invention features a method to produce substrates with biaxially textured surfaces by a sheath and core approach. A can of a sheath material consisting of Cu, Ni, CuNi and 0 to 3 atomic % of first oxide former is prepared. A core is prepared having 0 to 100 atomic %, and preferably 3 to 100 atomic % of a second oxide former, and nickel with the balance being copper. Preferably, the core includes from about 0 to about 45 atomic percent nickel, more preferably from about 0 to about 48 atomic percent nickel, and most preferably from about 0 to about 50 atomic percent nickel. When the magnetic properties of the core are less important, the nickel content of the alloy can be up to 60 atomic percent. The method includes placing the core in the can and co-reducing the combination to form an article. Planar deformation of the article is performed to a reduction in thickness between 85 and 99.9%, followed by heat treating the deformed article to develop a biaxial texture on the surface of the article. The substrate can optionally be annealed in a low oxygen partial pressure atmosphere to form an epitaxial oxide layer.

30 Variants of the sheath and core approach are based on a powder metallurgy or rolled foil approach. This is an alternative to melting the alloy, and offers advantages in processing capabilities and cost. A thinner can may be used in the powder metallurgy variant increasing the overall concentration of the second oxide

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former. For powder metallurgy, a powder mixture of 0 to 100 atomic % of a second oxide former and nickel with the balance being copper, is placed into a can or container having a composition as described for the general sheath and core method. Preferably, the powder mixture includes from about 0 to about 45 atomic percent nickel, more preferably from about 0 to about 48 atomic percent nickel, and most preferably from about 0 to about 50 atomic percent nickel. When the magnetic properties of the powder mixture are less important, the nickel content of the alloy can be up to 60 atomic percent.

A rolled foil approach uses individual foils of Cu, Ni, and a second oxide former or alloys thereof, which are stacked together and rolled together to form a bar, which is then used as a core material or a wrapping for a central core. Cores made in this manner are placed inside a can having a composition as described for the sheath and core method. Co-reduction, planar deformation, and heat treatment of the core and can are similar to that described for the general sheath and core process. Oxidation resistant substrates, with biaxially textured and preferably cube textured surfaces, are produced.

Preferred embodiments of the powder metallurgy and rolled foil approaches provide a method to strengthen the substrate material using internal oxidation. The method includes creating rolled foils or a powder mixture with a combined concentration of 3 to 50 atomic % of an oxide former and Ni with the balance being copper. Preferably, the alloy includes from about 0 to about 45 atomic percent nickel, more preferably from about 0 to about 48 atomic percent nickel, and most preferably from about 0 to about 50 atomic percent nickel. When the magnetic properties of the alloy are less important, the nickel content of the alloy can be up to 60 atomic percent. The

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Ni and Cu powders or foils contain a combined concentration of 0.2 to 1 weight % oxygen. The powder mixture or foils are placed into a can of composition as described for the sheath and core method and are co-  
5 reduced to form an article. Co-reduction, planar deformation, and heat treatment of the core and can are similar to that described for the general sheath and core process. Biaxially textured oxidation resistant substrates, preferably of a cube texture, are produced.  
10 A small amount of the oxide former absorbs the oxygen in the Ni and Cu powders to form oxide particles which strengthen the article. When any oxide former is internally oxidized into small oxide particles, a major strengthening effect is obtained. These small oxide  
15 particles, (between 0.002 and 1 micrometer in size) are extremely efficient in pinning the movement of dislocations, even when their volume percentage is as small as 0.2-0.5%. This internal oxidation method forms  
high strength alloy articles with biaxially textured  
20 surfaces in accordance with the invention, which are typically also oxidation resistant.

In another aspect of the invention, a substrate material has a controlled coefficient of thermal expansion (CTE) which makes it more compatible with the  
25 relatively low CTE of superconducting oxides. In a preferred embodiment, substrates with a biaxially textured surface, preferably a cube textured surface, high oxidation resistance and controlled CTEs are provided in accordance with previously described aspects  
30 of the invention. The substrates are produced by performing any of the above mentioned methods of the invention (i.e. the melt process, the sheath and core process, or the powder metallurgy, rolled foil, or the internal oxidation variants of the sheath and core  
35 process) or prior art substrate-forming processes, with



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the additional step of placing one or more rods of Nb, Ta, Ti, NbTi, NiAl, Ni<sub>3</sub>Al, V, Cr, Zr, Pd, Sb, or mixtures thereof in the core or billet. The rod preferably occupy between 5 and 40 volume % of the billet. The billet or  
5 core is processed according to the selected method into the final substrate and then heat treated. The substrate can optionally be annealed in a low oxygen partial pressure atmosphere to form an epitaxial oxide layer. This produces a substrate with a embedded low CTE rod  
10 which reduces the overall CTE of the substrate. In preferred embodiments, the overall CTE of the substrate has a value of about  $10-15 \times 10^{-6}/^{\circ}\text{C}$ .

A method to reduce the deleterious effect of surface groove formation during the texturing heat  
15 treatment is also provided according to the invention, as well as a substrate having improved surface smoothness. This method is utilized with prior art substrate-forming processes, or with any of the processes described above, by selecting and completing one of the processes to make  
20 a substrate, including the texturing anneal step. This method adds the additional steps of rolling the substrate formed by the selected process using no more than 3 low reduction passes and very smooth rolls, and then low temperature stress annealing the substrate in a  
25 protective atmosphere without recrystallization. This produces a substrate with a 5 to 50 nanometer Ra surface roughness.

In another aspect of the invention, a process for forming a superconducting composite begins by forming a  
30 substrate with biaxially textured and preferably cube textured surfaces from an alloy of 0.1 to 25 atomic % of an oxide former, nickel, and the balance being copper. Preferably, the alloy includes from about 0 to about 45 atomic percent nickel, more preferably from about 0 to  
35 about 48 atomic percent nickel, and most preferably from

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about 0 to about 50 atomic percent nickel. When the magnetic properties of the alloy are less important, the nickel content of the alloy can be up to 60 atomic percent. The substrate can optionally be annealed in a low oxygen partial pressure atmosphere to form an epitaxial oxide layer. The substrate is coated with a buffer layer, which is coated with a superconducting oxide.

A product, according to the invention, can be a superconducting composite having a substrate with biaxially textured, and preferably cube textured, surfaces formed from an alloy of 0.1 to 25 atomic % of an oxide former, nickel and the balance being copper. Preferably, the alloy includes from about 0 to about 45 atomic percent nickel, more preferably from about 0 to about 48 atomic percent nickel, and most preferably from about 0 to about 50 atomic percent nickel. When the magnetic properties of the alloy are less important, the nickel content of the alloy can be up to 60 atomic percent. The substrate can optionally be annealed in a low oxygen partial pressure atmosphere to form an epitaxial oxide layer. A buffer layer is coated on the substrate and a superconducting oxide layer is coated on the buffer layer.

25

#### Brief Description of the Drawings

These and other features of the invention will become more readily apparent from the following detailed description together with the accompanying drawings in which:

30

Fig. 1 is a block diagram illustrating a process of forming a biaxially textured alloy.

Fig. 2 is a block diagram illustrating a sheath and core approach for forming a biaxially textured alloy.

Fig. 2A illustrates foil rolling.

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Fig. 2B illustrates a rolled foil as a wrap material for a core.

Fig. 2C illustrates a rolled foil as a core for a can.

5 Fig. 3 is a block diagram illustrating a powder metallurgy variant of the sheath and core approach for forming a biaxially textured alloy.

Fig. 4 is a block diagram illustrating an oxide dispersion process for forming a biaxially textured  
10 alloy.

Fig. 5 is a block diagram illustrating a process for forming a biaxially textured alloy with a reduced thermal expansion coefficient.

Fig. 6 is a block diagram illustrating a process  
15 for forming a biaxially textured alloy with reduced surface grooving.

Fig. 7 illustrates a partial cross-sectional view of a substrate with a sheath and a powder metallurgy core.

20 Fig. 8 illustrates a partial cross-sectional view of a substrate with a sheath and a core.

Fig. 9 illustrates a partial cross-sectional view of a superconductor composite formed with a biaxially textured alloy substrate and textured buffer layer.

25 Fig. 9A and 9B illustrate partial cross-sectional views of a superconductor composite with multiple buffer layers.

Fig. 10 illustrates a partial cross sectional view of a composite similar to the one illustrated in  
30 conductor as in Fig. 9, in which the core includes a material with a low CTE.

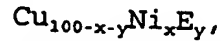
Fig. 11 illustrates a (111) pole figure of a cube textured alloy made in accordance with the invention.

#### Description of the Embodiments

35 The present invention features an alloy with a

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biaxial texture which has the following composition:



where the Ni content x is preferably from about 0 to about 45 atomic %, more preferably from about 0 to about 48 atomic %, and most preferably from about 0 to about 50 atomic %. When the magnetic properties of the composition are less important, the composition can include up to about 60 atomic % nickel. The content of oxide former can vary between 0.1 and 25 atomic %, with the balance 100-x-y being atomic copper. For Cu-Ni alloys, the enhanced Ni content achieves many of the desirable features in the alloy, such as an increased oxidation resistance, decreased CTE, and increased room temperature and high temperature strength.

The third alloying element, an oxide former, which is a stable oxide former, is preferably added to the binary CuNi alloy to give a ternary alloy having enhanced oxidation resistance. Alternatively, an oxide former E can be added to Cu without adding Ni. Further, a combination of various oxide formers E1, E2, E3 etc. can be used so long as the total of their concentrations does not exceed 25 atomic %. Suitable oxide formers which can be used with the present invention include Al, Mg, Ti, Cr, Ga, Ge, Zr, Hf, Be, Y, Si and the rare earth elements La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Th, and mixtures thereof, which form a protective scale on the alloy.

When the magnetic properties of the composition are relatively important, the upper limit of the atomic percentage of nickel (e.g., 50 atomic %) can be established to minimize the risk of developing ferromagnetic properties in the alloy which are detrimental to the superconducting properties of a supported superconducting oxide layer. Further, by remaining below this upper limit, a strong biaxial

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texture of the alloy can be maintained, which can allow the alloy to be advantageously used as a substrate for superconducting applications, even though small amounts of oxide former E are added to the Ni-Cu mixture. With  
5 the appropriate buffer layer material, the Cu-Ni alloy substrate does not adversely affect the superconducting properties of a supported layer E.

In certain embodiments, the alloy can include at least about one weight percent of the oxide former and  
10 still have a biaxially textured surface. In these embodiments, the article can include at least about two weight percent of the oxide former and/or at most about four weight percent of the oxide former.

In other embodiments, the invention features an  
15 alloy, or an article formed from the alloy, that includes copper and nickel, and has a native oxide exterior formed of alumina (i.e., the alumina exterior is grown by, for example, exposing the alloy to oxidizing conditions,  
rather than forming the alumina exterior by depositing  
20 alumina). In these embodiments, the alloy can have a biaxially textured surface, such as a cubic surface.

As described above, many metals and alloys with various structures can be biaxially textured, and a number of these have been of interest for use as  
25 substrate materials. A particular case are metals or alloys with the face centered cubic (fcc) structure, which have been processed to display a biaxial cube texture, often indicated by the crystallographic notation (100) [001]. These can typically be formed by sheet or  
30 tape rolling of a suitable metal or alloy, followed by an appropriate heat treatment. These textured alloys are particularly useful as substrate materials for superconducting composites, and such metals or alloys with a cube texture have crystallites in which the cube  
35 faces are parallel to a tape surface, while one cube edge

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of the parallel cube faces points in the rolling direction.

The effectiveness of the substrate is determined by the quality of the biaxial texture. For example, in a metal or alloy with a cube texture, the orientation of the cube oriented grains should be within a few degrees of the ideal orientation. Grains with an orientation which deviates substantially from the cube texture should be small in number, preferably below 15 volume %. The quality of these textures is revealed in their X-ray diffraction pole figures, which show the collective orientations of all crystallites in the irradiated area. Random orientations show no concentration of directions. Quality textures, on the other hand, show sharp peaks in the pole figures. The sharpness of these peaks is expressed as a Full Width Half Maximum (FWHM) value and is indicative of texture quality. The lower the FWHM value, the sharper the peak, and hence, the better the texture. For polycrystalline materials, a FWHM value of well below  $10^\circ$  is considered good. Higher FWHM values can be acceptable for substrate purposes, in particular if the reduced texture is offset by advantages in other areas, such as improved oxidation resistance, or better chemical or CTE compatibility. In general, alloy substrates result in FWHM values that are often higher than the FWHM values of the similarly treated pure metal constituents, but the alloying does lead to advantages as mentioned before, such as a non-magnetic substrate, improved oxidation resistance, improved CTE etc. For cube textured alloys of the present invention, FWHM values in the range of about  $6^\circ$  to about  $14^\circ$  may be obtained.

An example where a higher percentage of oxide former leads to a different, i.e., not cube, but still useful biaxial, texture is the annealed brass texture,

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often indicated by the notation (113)[211], and sometimes by (227)[734]. Both notations indicate the same biaxial texture in which the (113) or the nearly identical (227) plane is parallel to the rolling surface. Instead of a square cube face, the unit cell is now a square with distorted right angles. This distortion is about 5-6°, which is sufficiently low to make this texture useful for substrate purposes. The sides of this distorted square are 5-6% longer, which is advantageous for Cu, Ni or CuNi alloys where the actual lattice constant is about 10% short of the ideal.

In accordance with a preferred application of the substrates of the invention, superconducting composites are formed using the above described alloy articles with biaxially textured surfaces as substrates and by coating at least one surface of each substrate with a superconducting oxide. Preferably, a protective oxide scale is formed on the substrate prior to or during the coating process. The coating can include, for example, a superconducting oxide such as yttrium-barium-copper-oxide (YBCO) or a rare earth barium copper oxide (REBCO) or mixtures of the two classes, wherein the YBCO yttrium is partially or completely replaced by rare earth elements such as lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium and thorium. Other possible superconductor oxides include the mercury, bismuth, and thallium families. The coating of the superconducting oxide is preferably approximately 0.2 to 20 micrometers thick, more preferably 1-20 micrometers thick, and is applied by deposition techniques such as electroplating, non-vacuum solution deposition, chemical vapor deposition, physical vapor deposition techniques such as sputtering, laser ablation, thermal evaporation, electron beam evaporation, metallorganic or sol-gel

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solution precursor methods.

A preferred precursor approach uses a metallorganic trifluoroacetate precursor solution. With this approach, high temperature superconductor films are spun or dip coated onto substrates and then reacted to form the superconducting YBCO phase. The as-coated precursor includes an oxy-fluoride film containing  $\text{BaF}_2$ . Heat treatment in a controlled atmosphere, such as that disclosed in U.S. Patent No. 5,231,074 issued to Cima, et al., fully incorporated herein by reference, decomposes the  $\text{BaF}_2$  phase and thereby crystallizes the film. This allows the nucleation and growth of an epitaxial YBCO film. Superconductor oxide films characterized by highly textured morphologies and fully dense, homogenous microstructures are capable of sustaining critical current densities in excess of  $10^4 \text{ A/cm}^2$  at 77 degrees Kelvin when prepared on non-lattice matched substrates, and or critical current densities in excess of  $10^6 \text{ A/cm}^2$  at 77 degrees Kelvin when prepared on lattice matched substrates.

The surface characteristics of the substrate for receiving the superconducting oxide coating can be improved by depositing a buffer layer (or multiple buffer layers) in an epitaxial manner onto substrate. Any of the deposition processes listed above for the superconducting oxide can be used. Other methods are also available as is well known in the field. Alternatively, a buffer layer or part of a buffer layer can be grown epitaxially from the alloy articles of the present invention as a native oxide. Irrespective of how the buffer layer is created, the buffer layer preferably has a thickness of approximately 0.05 to 10 micrometers, more preferably 0.2 to 0.8 micrometers. It can include a single metal or oxide layer. The buffer layer can also be a multiple layered structure. Preferably, according



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to the invention, the resulting superconductive structure includes a biaxially textured substrate, on which a biaxially textured buffer layer is deposited, using an epitaxial deposition process, and onto which a biaxially textured superconducting layer is deposited, again using an epitaxial deposition process. A protective oxide scale grown from the substrate in accordance with one aspect of the invention may form all or part of a buffer layer.

10 The buffer layer and superconducting layer can be on one side or both sides of the substrate, and can partially or entirely surround the substrate. The buffer layer can be a metal layer or an oxide layer or combinations of metal layers and/or oxide layers. Each layer must provide the texture, chemical compatibility, 15 lattice constant, and proper CTE match for the underlying substrate. For example, the buffer layer can be a noble metal or noble metal alloy, or an oxide with a cubic structure such as  $\text{CeO}_2$ ,  $\text{Yb}_2\text{O}_3$ , or yttria-stabilized zirconia ("YSZ"), or any combination of oxides and/or 20 metals. Importantly, when the buffer layer or multiple buffer layers are deposited in an epitaxial process, the biaxial texture of the substrate is transferred onto each successive layer, and finally to the top layer which is 25 the YBCO or superconducting layer. A metal cap layer can be provided on top of the superconducting layer.

The metals useful for the buffer layer and cap layer are preferably noble metals or noble metal alloys. By "noble metal" is meant a metal which is 30 thermodynamically stable under the reaction conditions employed relative to the desired superconducting ceramic, and/or which does not react with the superconducting ceramic or its precursors under the conditions of manufacture of the composite. The noble metal can be a 35 metal different from the metallic matrix elements of the

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desired superconducting ceramic. The noble metal can be silver or a silver/gold alloy, but it can also be a stoichiometric excess of one of the metallic elements of the desired superconducting ceramic, such as yttrium.

5. Silver (Ag) and silver alloys are the most preferred noble metals. Other noble metals which can be used are platinum, gold, palladium, rhodium, iridium, ruthenium, rhenium, rhenium or alloys thereof. Suitable oxides such as MgO, cubic  $\text{Al}_2\text{O}_3$ , yttria, YSZ, or rare earth oxides  
10 such as  $\text{CeO}_2$ ,  $\text{Yb}_2\text{O}_3$ , etc. or mixtures of these are typically stable oxides with a cubic structure.

Fig. 9 illustrates a partial cross-sectional view of a superconducting composite structure 900 according to the invention. The composite 900 in which the substrate  
15 901 has a buffer layer 902 with a superconducting oxide layer 903 coated on at least one side thereof. Figure 9A illustrates a partial cross-sectional view of a superconducting composite structure where the buffer  
layer includes two layers 904 and 905. Layers 904 and  
20 905 can be metal or oxide layers or any combination of layers. A superconducting layer 903 is then deposited on layer 905. Alternatively, as shown in Figure 9B, the buffer layer can include three or more layers, in which the substrate 901 is coated with a metal or oxide layer  
25 ~~906 which in turn is coated with additional metal or~~  
oxide layers 907 and 908 before deposition of the superconducting layer 903.

Biaxially textured alloys of the present invention may be formed by several methods. These methods produce  
30 an alloy of Cu or CuNi to which one or more oxide formers (such as Al, Mg, Ti, Cr, Ga, Ge, Zr, Hf, Be, Y, Si, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th) are added. The substrates and alloy articles according to the invention can be manufactured using a  
35 number of different process, each having its own

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advantages. For example, the melting and sheath and core methods for creating alloy articles of the present invention are described with reference to Figures 1 and 2. Each of these methods is useful for forming substrates and can be used, with some variations in other processes, described in reference to Figures 3-6 and the examples which follow.

Referring to Figure 1, a block diagram illustrates a melt process 100 for forming a alloy article with a biaxially, and preferably cube textured surface. The alloy articles of the present invention are created by first selecting and weighing the constituent metals in a mixture an appropriate amount of nickel, 0.1 to 25 atomic % of an oxide former E (such as Al, Mg, Ti etc.), with the balance being copper (Step 101). Preferably, the alloy includes from about 0 to about 45 atomic % nickel, more preferably from about 0 to about 48 atomic % nickel, and most preferably from about 0 to about 50 atomic % nickel. When the magnetic properties of the alloy are less important, the alloy can include up to about 60 atomic % nickel. When a cube texture is desired the amounts of oxide former should not exceed 1-3 atomic %, depending on which oxide former is chosen. This mixture is then melted (Step 102) by various processes known in the art, such as arc melting, induction melting, melting in an electrical resistance furnace, or furnace heated by gas or coal. Melting temperatures range from 900°C to 1250°C. A certain level of homogenization is achieved during the melt process due to convection, mechanical stirring, or stirring induced by the melting techniques such as in an induction melter. The melting can optionally be preferred in air, or under a protective atmosphere such as nitrogen, argon, helium, high vacuum etc. Melting can be repeated a few times to further increase homogenization (Step 103). The melt is then

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cooled within the furnace and the solidified melt is shaped, preferably into a bar. The bar is reduced in diameter, by a factor of 1.3 to 5, by rolling, swaging, drawing or extrusion, and is then heat treated to further  
5 homogenize the alloy (Step 104). A further mechanical reduction in diameter, by similar mechanical techniques follows, to a size where the planar deformation process will commence (Step 105). Before or at this stage, a heat treatment can be applied to recrystallize the alloy  
10 and obtain a fine grain size of approximately 5 to 70 micrometers, preferably greater than 10 micrometers and less than 40 micrometers (also Step 105). Alternatively, other methods can be utilized to achieve a fine grain size, such as the rapid solidification of the alloy after  
15 melting. The alloy article is now deformed in an axially symmetric manner, such as, by extruding, swaging, drawing or rod rolling to a smaller size, which can be round, square, or rectangular (Step 106). Alternatively, the melt can be cast and rolled directly into a plate shape.  
20 The plate can be further homogenized with a suitable heat treatment, rolled to a thinner size, and recrystallized to induce a desired fine grain size.

The fine grained alloy article is then deformed further by various planar rolling methods known in the  
25 art (Step 107), to reduce the thickness of the stock by at least 85% but not more than 99.9%. A recrystallization anneal (Step 108) in a protective, e.g., high vacuum, low oxygen or reducing atmosphere, at temperatures exceeding 250°C but not more than 95% of the  
30 melting temperature, and preferably between 400 and 1200°C, produces the desired biaxial texture (100)[001]. The article is positioned to provide oxidation resistance during subsequent uses, such as during deposition of superconductor or buffer layers. Alternatively, the  
35 article may be annealed (Step 109) to form a protective

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epitaxial oxide layer.

Rolling processes suitable for use with methods of the present invention as shown in Figs 1 and 2, utilize the following parameters. Rolling is typically performed at room temperature, with a rolling speed of between 0.10m/minute and 100m/minute. The reduction schedule typically follows a constant strain per pass, with reduction steps being set at between 5 and 40% per pass. The resulting tape can be lubricated during rolling, or rolled without any lubricant. Bidirectional rolling is preferred. The tapes can be rolled with large diameter rolls (3.5 to 8" or larger in diameter) or with small diameter rolls (0.75" to 2" in diameter) which are preferably backed up by larger rolls, in a so-called four-high arrangement. An alternative to the four-high arrangement is the cluster rolling mill. A planetary rolling mill can be used as well.

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Referring to Figure 2, a block diagram illustrates a process 200 for forming a biaxially textured alloy with improved oxidation resistance, which uses a sheath and core approach. A sheath is biaxially textured, which, for example, can be a cube texture, while the core provides a high concentration of oxide former needed to provide the oxidation resistance during the subsequent

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buffer layer and superconductor deposition processes. For the sheath and core approach, a thick walled can (Step 201) is made of CuNi or Ni stock, or alternatively, of Cu, CuNi or Ni, with small (0.1 to 3 atomic %) additions of an oxide former E. The thickness of the wall is between about 5% and about 90% of the can outside radius. A core is made to fit inside the can using a melt process or one of the variations described below. (Step 202). The core includes nickel, alloyed with 0 to 100 atomic % of an oxide former E (such as Al, Mg, Ti, etc.), (preferably 3 to 100 atomic % of the oxide former

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E), and the balance copper.

In one variation, known as the "rolled foil" or "jelly roll" variation, as shown in Fig. 2A, individual foils 220a-220b of Cu, Ni, an oxide former or alloys thereof 220c, can be stacked together and rolled into a bar 222, a so called "jelly roll", which can be used as a core material or a wrapping for a central core. Aluminum is a particularly useful oxide former in making rolled foils, due to its deformability. In Fig. 2B, the rolled foil bar 222 is illustrated inside an outer layer of can 226 and is a wrap material for a core 228. In Fig. 2C, the rolled foil 222 is illustrated inside a can 226 process and is the core for the can.

Referring to Figure 3, a block diagram illustrates a process 300 for forming an alloy substrate with a biaxially textured surface and improved oxidation resistance, which uses a Powder Metallurgy variant of the sheath and core approach. This is one of the preferred embodiments of the general sheath and core method illustrated in Figure 2. A sheath is worked into the desired biaxial texture while a powder metallurgy core provides the high concentration of oxide former needed to provide the oxidation resistance during buffer layer and superconductor layer deposition. For this approach 300, a thick walled can (step 301) is made of Cu, CuNi or Ni stock, or alternatively, of Cu, CuNi or Ni with small (0.1 to 3 atomic %) additions of a first oxide former E as generally described in Step 301. The thickness of the wall is between about 5% and 20% of the can outside diameter. The can is filled with a mixture of elemental powders (step 302) or alternatively, pre-alloyed powders including 0 to 100 atomic % of one or more second oxide formers, nickel and the balance copper. Preferably, the alloy includes from about 0 to about 45 atomic % nickel, more preferably from about 0 to about 48 atomic % nickel,

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and most preferably from about 0 to about 50 atomic % nickel. When the magnetic properties of the alloy are less important, the alloy can include up to about 60 atomic % nickel. The oxide formers may be the same or different. The powder mixture is poured into the can at tap-density (Step 302), or is compacted into the can using a press with a compacting ram.

Each elemental or alloy powder should have the ability to deform well when consolidated into a powder mixture. The powders are then deformed to high areal reductions in order to form the substrate. Many elemental and alloyed fcc powders have been found to be well suited. Some hexagonal powders, such as Mg, are more difficult to deform and are easier to incorporate in the as-alloyed fcc solid solution, such as Cu-2 atomic % Mg. The same is true for an element such as, for example, Ga which is difficult to deform, but readily melts at ambient temperature processing. An alloy such as Cu-5 atomic % Ga has been found to deform very well up to high areal reductions; an atomized Cu-5 atomic % Ga powder has been found to be the ideal way to incorporate this element in the core of the substrate material. Other oxide formers, like Y, are also difficult to deform, and require deformation at elevated temperatures if an elemental incorporation is desired. The powder approach has more flexibility in choice of composition because the powder mixture can, in principle, have a very wide compositional range without adversely affecting the ability to mechanically deform the mixture. The advantage of the powder metallurgy approach is the reduced work hardening rate when using elemental powder mixtures for a core compared to the melt processed core approach. The compositional range of the powder core is larger than with the melt processed core approach, with 3 to 50 atomic % preferred.

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Cores formed by a melt process, by a powder metallurgy process, or by the rolled foil process of Figs. 2A-2C, are placed inside the can and the assembly is evacuated, sealed, and extruded, swaged, drawn, or  
5 rolled to a smaller cross sectional bar or tape (Step 203). This is processed further to a desired starting size to enable for the planar rolling to commence (Step 204). The resulting bar, wire, tape, sheet or foil is deformed in a planar manner such as rolling (Step 205),  
10 to a reduction in thickness of between 85% and 99.9%. A partial cross sectional view of the substrate 700 in this stage is shown in Fig. 7, with a powder metallurgy core 702 inside of a can 701. Example seven discusses the details of a process that uses a copper can and a Cu+37  
15 atomic % Al PM core. In Fig. 8 a partial cross-sectional view of a substrate 800, in this stage of the process, shows a core, such as a melt process core, 802 inside a sheath 801. A heat treatment (Step 206) follows in order to develop biaxial texture on the surface of the sheath,  
20 and to induce homogenization in the substrate. Temperatures can range from 250°C to as high as 95% of the melting temperature of the substrate. The oxide former will diffuse towards the surface of the substrate, but reach the surface after the biaxial texture has been  
25 developed on its surface. The enrichment of the surface layer with oxide formers will therefore not adversely affect the quality of the established cube texture. Upon diffusion, the oxide former is positioned to provide oxidation resistance during the subsequent buffer layers  
30 and superconductor deposition processes. Alternatively, the textured substrate can be annealed (Step 207) in a gas flow with a low oxygen partial pressure (typically between 0.01 and 5 vol% oxygen) to form an epitaxial oxide layer which is part of the buffer layer, or can  
35 serve as the buffer layer needed for the later



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superconductor deposition process.

When using a copper sheath, a recrystallization step at approximately 300°C remains possible before commencing the rolling, to refine the Cu grain size to 5 to 50 micrometers. The refined grain size is beneficial to obtain a cube texture in the rolled and heat treated tapes.

With small amounts of first oxide former (less than 1-3 atomic %) in the sheath, a same or different oxide former can be added in large concentrations (typically 3 to 25 atomic %) to the core. Sheaths without oxide formers may also be used. Pure elemental cores are also possible for certain oxide formers, such as Al, Yb, or Hf, Ce, Ti, Zr, or mixtures of these because of their deformation ability. A high quality biaxial, and in preferred embodiments, cube texture is obtained on the surface of the alloy article, where it is needed for the subsequent epitaxial deposition of buffer layers. The core supplies the oxide former, which diffuses from the core to the surface of the substrate after the texturing is completed, to form the protective oxide scale. This diffusion does not adversely affect the biaxial texture in the surface of the substrate. Some oxide formers, such as Al, form epitaxial cubic oxide layers at the surface, which can be successfully incorporated into the buffer layer, or even form the sole buffer layer of the superconducting composite.

Referring to Figure 4, a block diagram illustrates a process 400 for forming an alloy article with a biaxially textured surface and improved oxidation resistance, and which uses a variation on the powder metallurgy embodiment or the rolled foil embodiment of the sheath and core process. When selecting the starting powders or foils (Step 401), a Ni and/or Cu powder or foil is chosen that contains 0.2 to 1 weight % oxygen.

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Although Fig. 4 shows 0 to 60 atomic % nickel, other appropriate ranges of nickel can be used (e.g., 0 to 45 atomic %, 0 to 48 atomic % or 0 to 50 atomic %). Oxygen is often a common contaminant in commercial powders, especially Ni powders which often have an oxygen content of around 0.6 weight %. The presence of oxygen can be exploited by using it for the internal oxidation of some of the oxide formers. Additional powders or foils, such as an oxide former which is easily deformable, or a pre-alloyed Cu powder or foil, is selected for a total concentration, with the oxygen-containing powders or foils, of 3 to 50 atomic % oxide former, and the balance copper (Step 402). The composite is to be processed with the oxygen-containing starting powders or foils. For example, a Cu can is packed with a powder mixture that includes 60 atomic % Cu-25 atomic % Ni-15 atomic % Al, all in elemental powder form. The Ni powder contains 0.6 weight % oxygen, and the oxygen in the Cu and Al powder is negligible. The processing is similar to the approach illustrated in Figure 200, except that intermediate anneals are not recommended to avoid premature hardening of the substrate material (Step 403). During the final heat treatment (Step 404) at temperatures which can range from 250°C to as high as 95% of the melting temperature of the substrate, the oxygen reacts to binds with a portion of the oxide former to form an oxide dispersion strengthened alloy. Thus, in the example, a small percentage of the Al is used to bind the oxygen in the Ni powder into  $Al_2O_3$  to strengthen the substrate. Any remaining Al which is available enhances the oxidation resistance of the substrate. These oxide particles generally occupy 0.2 to 2 vol % of the core material. For this type of strengthening, also known as oxide dispersion strengthening, the result provides a sufficiently large volume percentage of oxide particles

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to significantly enhance both the room temperature and high temperature strength of the substrate. Both types of strength enhancement are important; room temperature handling of the substrate, high temperature handling during the various deposition processes, and then room temperature handling of the final coated conductor in subsequent cabling or winding operations.

Referring to Figure 5, a block diagram illustrates a process 500 for forming an alloy with a biaxially textured surface and an improved CTE matches among the substrate, the buffer layer, and the superconductor layer. The CTE of YBCO, for example, depends strongly on its crystallographic orientation. In the a-axis direction, the CTE of YBCO at room temperature is approximately  $11 \times 10^{-6} / ^\circ\text{C}$ , in the b-axis approximately  $8 \times 10^{-6} / ^\circ\text{C}$ , and in the c-axis direction, approximately  $18 \times 10^{-6} / ^\circ\text{C}$ . Most thin film deposition techniques are geared towards depositing a film with the c-axis perpendicular to the film surface, so the CTE in this direction is of less importance. That means that substrates need to be matched to the much lower CTE values of YBCO in the a and b direction. Ni has a CTE of  $13.5 \times 10^{-6} / ^\circ\text{C}$  and Cu of  $17 \times 10^{-6} / ^\circ\text{C}$ . These metals, being cubic, have the same CTEs for the a, b, and c axes which are isotropic. This means that both metals place a compressive strain on the YBCO layer when the sample is cooled from the reaction or deposition temperature (which can range from  $650^\circ\text{C}$  to  $850^\circ\text{C}$ , depending on the deposition process) to cryogenic temperatures. In the IBAD process, which uses a nickel-chromium alloy substrate with a CTE that is comparable to that of Ni, the compressive strain is about 0.5%. When using elements with a higher CTE such as Cu ( $17 \times 10^{-6} / ^\circ\text{C}$ ) or Ag ( $19 \times 10^{-6} / ^\circ\text{C}$ ), the compressive strain exceeds 0.5% by a considerable margin, and the risk of spalling and crack formation in the ceramic layer

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becomes unacceptable. Whenever a considerable mismatch exists between the CTE of the primary substrate material and either the superconducting layer or the buffer layer, the high CTE, of the substrate can be reduced by

5 incorporating into the alloy another element with a much lower CTE, such as Nb, Mo, Ta, V, Cr, Zr, Pd, Sb, NbTi, an intermetallic such as NiAl or Ni<sub>3</sub>Al, or mixtures thereof, but these materials do not typically alloy or texture as desired for high temperature superconductor

10 applications. In accordance with the invention, the CTE-reducing material is preferably included as a rod embedded in the alloy. In one embodiment multiple CTE-reducing rods may be used. Nb and NbTi are preferred elements because they are quite ductile, and can be

15 deformed in a Cu matrix. The effect is roughly proportional to the volume of the Nb or NbTi, but at elevated temperatures, when the Cu or CuNi begins yielding at very low strains, the influence of the work

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20 hardened Nb is even stronger as Nb does not recrystallize at temperatures below 1100°C. In other words, only a small amount of Nb (CTE:  $7.5 \times 10^{-6}/^{\circ}\text{C}$ ) is needed in the substrate to make it an effective CTE reducing agent. Typically the rod of CTE reducing material occupies 5 to 40 vol% of the billet, with 10-20% being preferred. In

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25 accordance with the invention, an oxide former, such as Al or Mg, is included in the alloy that surrounds the CTE-reducing rod to provide oxidation protection for the rod during the buffer layer and superconductor layer deposition processes. This approach to reduce the

30 overall CTE of the substrate can be used in any of the substrate-forming processes discussed above (Step 501) or in the prior art processes for forming superconducting substrates.

In a preferred embodiment of the invention, one or

35 more rods of a CTE-reducing material are placed in one or

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more bores in the billet for process 100, or in the core of the composite billet for processes 200, 300 or 400 (Step 502). The billet is processed into the final substrate according to any of processes 100-400 (Step 5 503) with a standard texturing heat treatment. The final substrate includes one or more rods of CTE-reducing material which reduce the overall CTE of the substrate, to preferably about  $10\text{-}15 \times 10^{-6}/^{\circ}\text{C}$ , the exact value depending on the composition and the volume % of the 10 rods. However, because the rods are located inside the substrate they do not impair any biaxial texture which is developed on the surface of the substrate by the process of the invention. An illustration of a partial cross section of a substrate produced by this process is shown 15 in Fig. 10. In this figure, the center includes a rod of CTE reducing material 1004, such as Nb, surrounded by the substrate material 1001. A buffer layer 1002 completely surrounds the substrate material 1001 and has a superconducting layer 1003 on at least one side. In one 20 embodiment, the rod can be coated with a thin layer, such as gold, which can prevent a reaction between the rod and an alloy in the core.

Referring to Figure 6, a block diagram illustrates a process 600 for forming a biaxially textured alloy with 25 improved surface smoothness it may be used as a final step to smooth the substrate before commencing the buffer layer deposition or coating superconductor. The surface smoothness of the substrate is desirable aspect in the deposition of a smooth, exclusively c-axis oriented 30 superconducting film (that is, with the c-axis normal to the substrate surface), and has been shown to be essential for YBCO films. If the surface roughness exceeds 3-7 nm Ra the current carrying capability of the film is strongly reduced. Rolling of substrate materials 35 as described heretofore can produce a very smooth

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surface, well within the 10 nm roughness range. The heat treatment to bring out the texture however, nearly always results in groove formation at the surface, located at the grain boundaries. The grooving is conceivably caused  
5 by surface tension, which is reduced by a curved grain at the surface, or by a diffusion of vacancies towards this region in the surface. The grooving, often referred to as "thermal grooving" results in a surface roughness that can often exceed 100 nm Ra. Methods to remove these  
10 grooves, such as mechanical or electro-polishing of the substrate, remove substrate material as well, and can lead to a loss in dimensional control.

In accordance with the aspect of the invention, a low reduction rolling pass, following a recrystallization  
15 heat treatment, restores the original surface smoothness, while a low temperature stress anneal, at temperatures below the recrystallization anneal, restores the high quality biaxial texture to the surface of the substrate.

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Any of the five processes 100-500 or a prior art  
20 substrate forming process can be selected to make a substrate with reduced surface grooving. The selected process is first entirely completed, including the texturing anneal (if any) (Step 601). The substrate is subsequently rolled once or twice (Step 602) using a  
25 reduction per pass of 5-30%, with rolls having an extremely fine finish, such as tungsten carbide with a 25-50 nm Ra surface roughness, or chromium-plated steel rolls with a 5 nm Ra surface roughness. The substrate is then given a low temperature stress anneal (Step 603), in  
30 a protective environment which does not lead to a recrystallization. A temperature range of 200-400°C is typical. The resulting substrate has a very smooth surface with a 5 to 50 nm Ra surface roughness and a well developed, undisturbed, and well-preserved biaxial  
35 texture.

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The following examples illustrate several particularly preferred processes and structures according to the invention.

#### Example 1

5       Copper metal of sufficient purity such as Electrolytic Tough Pitch or Oxygen Free High Conductivity Cu, Ni metal with a purity of more than 99%, Al metal with a purity of more than 98%, and Hf and Ti metals with a purity of more than 98% are weighed to obtain a Cu-16  
10 atomic % Ni-0.5 atomic % Al-0.05 atomic % Hf-0.05 atomic % Ti mixture. The metals are in the form of powder, chip, pellet, chunk, or rod, and enclosing can. The weighed Cu, Ni, Al, Hf and Ti are put in a suitable refractory crucible such as (but not limited to) alumina  
15 or zirconia, and are melted together. For a clean melt, an induction melter can be used, in which the melting is done in vacuum or in a protective atmosphere, but melting  
in air, and/or melting using other heater types such as arc melting or the use of resistance furnaces are  
20 possible. The alloy is remelted two or three times to ensure additional compositional homogeneity. The melting temperature is 1105°C. The cast is cleaned, and deformed by rolling, swaging or extrusion to a smaller diameter with sufficient size to allow subsequent deformation  
25 processing. At this size, it is again homogenized by holding the alloy at elevated temperatures for a few hours to a few days, depending on temperature. Effective temperatures should exceed 700°C. A preferable combination is 12 hrs at 1000°C. The alloy bar is then  
30 deformed by rod rolling, swaging, wire drawing or extrusion to a smaller size, which is typically round or rectangular in cross section, but can be oval or square as well. All of these different cross sections have been demonstrated to be equally effective for further  
35 processing. The thinnest dimension typically varies

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between 1mm and 10mm. The alloy wire, rod, tape or strip is then rolled to a thin tape or foil. The reduction in thickness is larger than 80% and can be as high as 99.9%.

One example is the extrusion of a homogenized 30.5mm or  
5 15.7mm diameter bar to a 3.8 mm x 2mm tape. The tape is rolled to 37 micrometers, a reduction in thickness of 98.1%. Another example is the swaging of a bar to a diameter of 6.2mm and subsequent rolling to a thickness of 250 microns, a reduction in thickness by rolling of  
10 96.0%. The rolling is performed with a conventional wire flattening mill. A wide variety of rolling conditions have been used successfully. For example, we have rolled the CuNi based substrate materials at 5%, 10%, 20% and 40% deformation per pass, using various lubrication  
15 schemes, and at speeds as low as 0.1 meter per minute or as fast as 100 meters per minute. In general, the lower reductions per pass and lower processing speeds result in somewhat improved textures.

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The texturing anneal can be performed using a wide  
20 range of temperatures, ranging from 250°C to close to the melting temperature of the alloy (around 1105°C). The higher temperatures require a shorter time and lead to slightly better textures, but can increase surface irregularities at the grain boundaries. This effect,  
25 also known as thermal grooving, leads to depressions in the surface at the grain boundaries due to surface tension effects, and is undesired for high quality buffer layers and superconducting layers. Lower temperature anneals have a much lower rate of thermal grooving, but  
30 also a less well developed texture. The temperature range of 850-1000°C, for a period of 1 to 24 hrs, and using a vacuum or protective atmosphere to avoid oxidation of the substrate, are preferred conditions. This process results in a substrate with a cube texture  
35 and no substantial secondary textures, a FWHM value of 7-



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9°.

The resulting thermal grooving is eliminated with the following processing step. The texture annealed tape is rolled once using very smooth rolls, typically with a surface roughness of about 5 nm Ra, to a reduction of 5% to 20%, with 10% being preferred. The substrate is then stress annealed at low temperatures, 300°C being preferred for the CuNi alloys, under protective atmosphere such as a vacuum. This procedure does not adversely affect the texture quality, or may improve it. It greatly enhances the surface smoothness of the substrate material, improving it to better than 5 nm Ra. The substrate is then ready for the next step in the superconductor manufacturing process, typically the application of a buffer layer.

#### Example 2

Electrolytic Tough Pitch copper, nickel with a purity greater than 99% aluminum with a purity greater than 98% and hafnium and titanium with a purity greater than 98% are weighed to obtain mixture containing 26.5 atomic % nickel, 0.5 atomic % aluminum, 0.05 atomic % titanium, and 0.05 atomic % hafnium with the balance copper. The weighed metals are placed in an alumina crucible. To insure a clean melt the charge is vacuum induction melted at 1250° Celsius and a vacuum of 50 millitorr, and cooled to room temperature. The alloy is melted two more times to insure material homogeneity. The melt is allowed to cool slowly, under vacuum, to minimize voids due to shrinkage. The cast billet is 33 mm in diameter by 75 mm long. The billet is machined to 31.8 mm diameter to improve surface finish. The machined billet is swaged to 16.8 mm diameter. After swaging the billet is homogenized at 950° Celsius for 24 hours in a protective argon 5% hydrogen reducing atmosphere. After homogenization the billet is machined to 15.6 mm and

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hydrostatically extruded to a tape with a 2 mm by 3.8 mm cross-section. The tape is then rolled with a constant reduction of 0.127 mm per pass to 0.051 mm final thickness, the reduction of the final pass being adjusted  
5 as required to achieve the desired thickness. The rolling is done on a four high wire flattening mill with 25 mm diameter work rolls and a speed of 3m per minute. The finished tape is then annealed at 850° Celsius for 4  
10 hours in a protective argon 5% hydrogen reducing atmosphere. This process produces a tape having a cube texture d surface with a FWHM of 12°, and no substantial secondary texture.

### Example 3

Electrolytic Tough Pitch copper, nickel with a  
15 purity greater than 99% and aluminum with a purity of greater than 98% are weighed to obtain a mixture containing 37 atomic % nickel, 0.5 atomic % aluminum, with the balance copper. The weighed metals are placed  
in an alumina crucible. To insure a clean melt the  
20 charge is vacuum induction melted at 1280° Celsius and a vacuum of 50 millitorr, and cooled to room temperature. The alloy is melted two more times to insure material homogeneity. The melt is allowed to cool slowly, under vacuum, to minimize voids due to shrinkage. The cast  
25 billet is 33 mm in diameter by 75 mm long. The billet is machined to 31.8 mm diameter to improve surface finish. The machined billet is swaged to 16.8 mm diameter. After swaging the billet is homogenized at 1000° Celsius for 24  
hours in a protective argon 5% hydrogen reducing  
30 atmosphere. After homogenization the billet is machined to 15.6 mm and hydrostatically extruded to a tape with a 1.52 mm by 3.8 mm cross-section. The tape is then rolled with a constant reduction of 0.127 mm per pass to 0.061  
mm final thickness, the reduction of the final pass being  
35 adjusted to achieve the desired thickness. The rolling

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is done on a four high wire flattening mill with 25 mm diameter work rolls and a speed of 3m per minute. The finished tape is then annealed at 850° Celsius for 4 hours in a argon 5% hydrogen atmosphere. This process  
5 produces a tape and a cube textured surface with a FWHM of 14°, and no substantial secondary texture. Figure 11 shows the (111) pole figure for this material.

#### Example 4

An alloy comprising Cu-1.2 atomic % Al is made  
10 according to example 1. The alloy is made into a 16 mm round bar, and is drilled along the axis to create a bore in order to accommodate a 9.5 mm diameter Nb rod. This CuAl+Nb composite billet is extruded to a 3.2 mm diameter round extrudate, and subsequently drawn and rolled to  
15 achieve a 97% reduction in thickness. An anneal at 850°C yields a biaxially textured substrate. The Nb core does not interfere with the surface texture of the substrate.  
The CTE for this composite material is measured to be  
13.4x10<sup>-6</sup>/°C at room temperature. In the extruded  
20 material, the volume % of the Nb in the composite is determined to be 37.6 volume %. This percentage yields a calculated average CTE of 13.4x10<sup>-6</sup>/°C using the Rule of Mixtures, confirming the measured value. The Rule of Mixtures predicts that the CTE of a composite material is  
25 the average of the CTE of its components (which are 17.0x10<sup>-6</sup>/°C for CuAl and 7.5x10<sup>-6</sup>/°C for Nb), taking into account their relative volume percentages. This demonstrates that the CTE of a substrate can be carefully adjusted to provide an improved CTE match with the buffer  
30 layer and superconducting layer.

#### Example 5

Electrolytic Tough Pitch copper with a purity greater than 99% and aluminum with a purity of greater than 98% are weighed to obtain a mixture containing 9  
35 atomic % aluminum, with the balance copper. The weighed

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metals are placed in an alumina crucible. To insure a clean melt the charge is vacuum induction melted at 1100° Celsius and a vacuum of 50 millitorr, and cooled to room temperature. The alloy is melted to more times to insure material homogeneity. The melt is allowed to cool slowly, under vacuum, to minimize voids due to shrinkage. The cast billet is 33 mm in diameter by 75 mm long. The billet is machined to 31.8 mm diameter to improve surface finish. The machined billet is swaged to 16.8 mm diameter. After swaging the billet is homogenized at 950° Celsius for 24 hours in a protective argon 5% hydrogen reducing atmosphere. After homogenization the billet is machined to 15.6 mm and hydrostatically extruded to a tape with a 1.52 mm by 3.8 mm cross-section. The tape is then rolled with a constant reduction of 0.127 mm per pass to 0.061 mm final thickness. the reduction of the final pass being adjusted to achieve the desired thickness. The rolling is done on a four high wire flattening mill with 25 mm diameter work rolls and a speed of 3m per minute. The finished tape is then annealed at 850° Celsius for 4 hours in a protective argon 5%hydrogen reducing atmosphere. The finished substrate is heat treated at 830° Celsius using an oxidizing environment selected to be typical of the environment utilized during one YBCO deposition process, which is argon 1 vol oxygen gas, followed by a 100% oxygen anneal at 400° Celsius. The thin 40 micrometer thick substrate retains a biaxial surface texture and is protected from the oxidizing environment by the formation of a continuous native oxide film.

#### Example 6

Electrolytic Tough Pitch copper with a purity greater than 99% aluminum with a purity of greater than 98% are weighed to obtain a mixture containing 5 atomic %

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aluminum, with the balance copper. The weighed metals are placed in an alumina crucible. To insure a clean melt the charge is vacuum induction melted at 1080° Celsius and a vacuum of 50 millitorr, and cooled to room temperature. The alloy is melted two more times to insure material homogeneity. The melt is allowed to cool slowly, under vacuum, to minimize voids due to shrinkage. The cast billet is 33 mm in diameter by 75 mm long. The billet is machined to 31.8 mm diameter to improve surface finish. The machined billet is swaged to 16.8 mm diameter. After swaging the billet is homogenized at 950° Celsius for 24 hours in a argon 5% hydrogen atmosphere. After homogenization the billet is machined to 15.6 mm and hydrostatically extruded to a tape with a 1.52 mm by 3.8 mm cross-section. The tape is then rolled with a constant reduction of 0.127 mm per pass to 0.061 mm final thickness, the reduction of the final pass being adjusted to achieve the desired thickness. The rolling is done on a four high wire flattening mill with 25 mm diameter work rolls and a speed of 3m per minute. The finished tape is then annealed at 850° Celsius for 4 hours in an argon 5% hydrogen atmosphere. The finished substrate is heat treated at 830° Celsius using an oxidizing environment selected to be typical of the environment utilized during one YBCO deposition process, which is argon 1 vol% oxygen gas, followed by a 100% oxygen anneal at 400° Celsius. The thin 40 micrometer thick substrate retains a biaxial surface texture and is protected from the oxidizing environment by the formation of a continuous native oxide film.

#### Example 7

A Cu-14.4 atomic % Al alloy is made using a powder metallurgy sheath and core approach. A copper powder made from electrolytic tough pitch copper, with a particle size of 250 micrometers, and an aluminum powder

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made by gas atomization, with a purity of 99%, and a particle size of 220 micrometers, are mixed in a ratio of 63 atomic % Cu and 37 atomic % Al. The well-mixed Cu+Al powder is compacted into an oxygen free high conductivity  
5 copper billet which has an external diameter of 30.5 mm and an internal diameter of 21.5 mm. The billet is evacuated and extruded to a 9 mm bar. The bar is drawn through round and rectangular drawing dies to a final dimension of 2.4 mm x 3.6 mm. This rectangular product  
10 is subsequently rolled to a tape of 65 microns thick (97.3 % reduction). This tape is two-step annealed at 600°C and 800°C under protective atmosphere. This yields a Cu 14.4 atomic % Al substrate with a cube textured surface, which has excellent oxidation resistance.

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What is claimed is:

1. An alloy with biaxially textured surfaces comprising,  
about 0.1 to about 25 atomic % of an oxide former  
5 selected from the group consisting of Mg, Al, Ti, Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu, Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La, and mixtures thereof;  
about zero to about 60 atomic % nickel; and  
the balance being copper.
- 10 2. An alloy according to claim 1 with a cube textured surface.
3. A superconducting composite comprising,  
a substrate having cube textured surfaces and  
comprising an alloy of  
15 about 0.1 to about 25 atomic % of an oxide  
~~former selected from the group consisting of Mg, Al, Ti,~~  
Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu,  
Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La, and mixtures thereof,  
about zero to about 60 atomic % nickel, and  
20 the balance being copper; and  
a superconducting oxide coated on at least one  
surface of said substrate.
4. The superconducting composite of claim 3  
wherein the superconducting oxide is a rare earth  
25 superconducting copper oxide, a yttrium-barium-copper  
superconducting oxide, or mixtures thereof.
5. The superconducting composite of claim 3  
wherein said superconducting oxide coating has a  
thickness of approximately 0.2 micrometer to 20  
30 micrometers.

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6. A superconducting composite comprising,  
a substrate having cube textured surfaces and  
comprising  
an alloy of
- 5 about 0.1 to about 25 atomic % of an oxide  
former selected from the group consisting of Mg, Al, Ti,  
Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu,  
Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La, and mixtures thereof,  
about zero to about 60 atomic % nickel, and  
10 the balance being copper;  
a buffer layer coated on said substrate, and  
a superconducting oxide coated on said buffer  
layer.
7. The superconducting composite of claim 6  
15 wherein the superconducting oxide is a rare earth  
superconducting copper oxide, a yttrium-barium-copper  
superconducting oxide, or mixtures thereof.
- 
8. The superconducting composite of claim 6  
wherein said superconducting oxide coating has a  
20 thickness of approximately 0.2 micrometer to 20  
micrometers.
- 
9. The superconducting composite of claim 6  
wherein said buffer layer has a thickness of  
approximately 0.05 micrometer to 10 micrometers.
- 
- 25 10. The superconducting composite of claim 6  
wherein said buffer layer is deposited on said substrate  
in an epitaxial manner.
11. The superconducting composite of claim 6  
wherein said buffer layer is comprised of at least two  
30 layers of material.



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12. The superconducting composite of claim 6 wherein said buffer layer comprises a protective oxide scale of said oxide former.

13. A process for forming an alloy article with  
5 bi-axially textured surfaces comprising the steps of:

creating a mixture of

about 0.1 to about 25 atomic % of an oxide former selected from the group consisting of Mg, Al, Ti, Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu,  
10 Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La, and mixtures thereof, about 0 to about 60 atomic % nickel, and with the balance being copper;

melting said mixture;

solidifying said melted mixture to form an alloy  
15 article;

deforming said alloy article thickness by  
mechanical techniques; and

heat treating said deformed alloy article to develop biaxial texture.

20 14. The process of claim 13 further comprising the step of remelting said mixture after said melting step to enhance homogeneity.

15. The process of claim 13 further comprising the step of heat treating said alloy article to enhance  
25 homogeneity after said solidifying step.

16. The process of claim 13 wherein said deforming step reduces said alloy article thickness by more than 85% and up to 99.9% of the thickness of said alloy article.

30 17. The process of claim 13 wherein said

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texturing heat treating step is performed at a temperature greater than 250 degrees Celsius and up to 95% of the melting temperature of the alloy.

18. The process of claim 17 further comprising  
5 the step of annealing said alloy article in a low oxygen partial pressure atmosphere after said heating step to form a protective oxide scale.

19. The process of claim 13 further comprising the steps of:  
10 rolling said deformed and textured alloy article;  
and  
annealing said rolled alloy article without recrystallization to achieve a 5 to 50 nanometer Ra surface roughness.

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15 20. A product formed by the process of claim 13.

21. A process for forming an alloy article with bi-axially textured surfaces comprising the steps of:  
preparing a can of copper, nickel, or copper-nickel and about 0 to about 3 atomic % of a first oxide  
20 former selected from the group consisting of Mg, Al, Ti, Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu, Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La, and mixtures thereof;  
preparing a core comprising  
about 0 to about 100 atomic % of a second  
25 oxide former selected from the group consisting of Mg, Al, Ti, Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu, Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La, and mixtures thereof, and  
about 0 to about 60 atomic % nickel,  
30 with the balance being copper;  
placing said core in said can;

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co-reducing said core and said can to form an alloy article;  
planar deforming said alloy article; and  
heat treating said planar deformed alloy article  
5 to develop a surface biaxial texture.

22. The process of claim 21 wherein the step of preparing said core includes the steps of:  
creating a mixture of:  
about 3 to about 100 atomic % of said second  
10 oxide former and  
about 0 to about 60 atomic % nickel,  
with the balance being copper;  
melting said mixture to form an alloy;  
solidifying said alloy; and  
15 deforming said solidified alloy by mechanical techniques to shape a core.

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23. The process of claim 21 wherein the step of preparing said core includes the step of:  
creating a powder mixture of:  
20 about 0 to about 100 atomic % of said second oxide former, and  
about 0 to about 60 atomic % nickel,  
with the balance being copper; and  
the step of placing said core in said can includes  
25 the step of placing said mixture in said can.

24. The process of claim 21 wherein the step of preparing said core includes the steps of  
creating a stack comprising a plurality of foils  
consisting of copper, nickel, oxide formers or alloys  
30 thereof, and  
rolling said stack to form a bar, and  
wherein the step of placing said core in said can

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includes the step of placing said bar in said can.

25. The process of claim 21 wherein the step of preparing said core includes the steps of

creating a stack comprising a plurality of foils  
5 consisting of copper, nickel, oxide formers or alloys thereof,

forming a central core comprising Cu, Ni, or a mixture thereof, and

rolling said stack around said central core to  
10 form a wrapped core, and

wherein the step of placing said core in said can includes the step of placing said wrapped core in said can.

26. The process of claim 21 wherein said planar  
15 deforming step reduces said alloy article by more than 85 and up to 99.9% of the thickness of said alloy article.

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27. The process of claim 21 further comprising the step of annealing said alloy article in a low oxygen partial pressure atmosphere after said heat treating step  
20 to form a protective oxide scale.

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28. The process of claim 21 wherein said core includes an oxide former in an amount of 3 to 25 atomic %.

29. The process of claim 21 wherein said core  
25 includes an oxide former selected from Al, Yb, Hf, Ce, Ti, Zr, or mixtures thereof in an amount of 100 atomic %.

30. The process of claim 21 wherein said can comprises 0 to 45 atomic % nickel with the balance being copper.

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31. The process of claim 21 further comprising the steps of rolling said deformed and textured alloy article; and

annealing said rolled alloy article without  
5 recrystallization to achieve a 5 to 50 nanometer Ra surface roughness.

32. The process of claim 23 wherein said second oxide former comprises 3 to 50 atomic % of said powder mixture and said nickel and said copper in said powder  
10 mixture have a combined concentration of 0.2 to 1 weight % oxygen, and

wherein the process further comprises the step of reacting the oxygen with a portion of the oxide former during the texturing heat treatment to form a core with  
15 0.2 to 2 volume % oxide particles.

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33. The process of claim 24 wherein  
said second oxide former comprises 3 to 50 atomic % of said plurality of foils, and

said plurality of foils includes one or more foils  
20 consisting of 0.2 to 1 weight % oxygen in Ni, Cu, or an alloy consisting of Cu and Ni, and

wherein the process further comprises the step of  
reacting the oxygen with a portion of the oxide former  
during the texturing heat treatment to form a core with  
25 0.2 to 2 volume % oxide particles.

34. The process of claim 25 wherein  
said second oxide former comprises 3 to 50 atomic % of said plurality of foils and said central core in combination, and

30 wherein said central core have a combined concentration 0.2 to 1 weight % oxygen, and

wherein the process further comprises the step of

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reacting the oxygen with a portion of the oxide former during the texturing heat treatment to form a core with 0.2 to 2 volume % oxide particles.

35. A product formed by the process of claim 21.

5 36. A product formed by the process of claim 22.

37. A product formed by the process of claim 23.

38. A product formed by the process of claim 24.

39. A product formed by the process of claim 25.

40. A process for forming a superconducting  
10 composite comprising the steps of:  
forming a substrate having cube textured surfaces  
from an alloy of

about 0.1 to about 25 atomic % of an oxide  
former selected from the group consisting of Mg, Al, Ti,  
15 Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu,  
Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La, and mixtures thereof,  
and

about zero to about 60 atomic % nickel, with  
the balance being copper; and  
20 coating said substrate with a superconducting  
oxide on at least one surface thereof.

41. The process of claim 40 wherein the  
superconducting oxide is a rare earth superconducting  
copper oxide, a yttrium-barium-copper superconducting  
25 oxide, or mixtures thereof.

42. The process of claim 40 wherein said  
superconducting oxide is coated in a thickness of

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approximately 0.2 micrometer to 20 micrometers.

43. A process for forming a superconducting composite comprising the steps of:

forming a substrate having cube textured  
5 surfaces from an alloy of

about 0.1 to about 25 atomic % of an oxide  
former selected from the group consisting of Mg, Al, Ti,  
Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu,  
Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La, and mixtures thereof,  
10 and

about zero to about 60 atomic % nickel, with  
the balance being copper;  
coating a buffer layer on said substrate, and  
coating a superconducting oxide on said  
15 buffer layer to form a superconducting oxide layer.

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44. The process of claim 43 wherein the  
superconducting oxide is a rare earth superconducting  
copper oxide, a yttrium-barium-copper superconducting  
oxide, or a mixture thereof.

20 45. The process of claim 43 wherein said  
superconducting oxide layer has a thickness of  
approximately 0.2 micrometer to 20 micrometers.

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46. The process of claim 43 wherein said buffer  
layer has a thickness of approximately 0.05 micrometer to  
25 10 micrometers.

47. The process of claim 43 wherein said buffer  
layer is deposited on said substrate in an epitaxial  
manner.

48. The process of claim 43 wherein said buffer

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layer is comprised of at least two layers of material.

49. The process of claim 43 wherein said buffer layer comprises a protective oxide scale of said oxide former.

5 50. A process for forming an alloy article with bi-axially textured surfaces comprising the steps of, creating a mixture of:

about 0.1 to about 25 atomic % of an oxide former selected from the group consisting of Mg, Al, Ti,  
10 Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu, Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La, and mixtures thereof, about 0 to about 60 atomic % nickel, and with the balance being copper;

melting said mixture;  
15 solidifying said melted mixture to form an alloy article;

creating a bore in said alloy article;  
placing a rod of CTE - reducing material selected from the group consisting of Nb, Ta, Ti, NbTi, NiAl,  
20 Ni<sub>3</sub>Al, V, Cr, Zr, Pd, Sb and mixtures thereof into said bore;

deforming said alloy article and said rod by mechanical techniques; and  
heat treating said deformed alloy article to  
25 produce a biaxial texture.

51. The process of claim 50 further comprising the steps of:

rolling said alloy; and  
annealing said rolled alloy without  
30 recrystallization to achieve a 5 to 50 nanometer Ra surface roughness.



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52. The process of claim 50 comprising the steps of creating a plurality of said bores and placing a plurality of said rods in said bores.

53. A product formed by the process of claim 50.

5 54. A process for producing an alloy article with biaxially textured surface comprising the steps of:

preparing a core comprising

about 0 to about 100 atomic % of a second oxide former selected from the group consisting of Mg,  
10 Al, Ti, Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu, Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La, and mixtures thereof,

about 0 to about 60 atomic % nickel, and with the balance being copper;

15 preparing a can of copper, nickel or copper-nickel and about 0 to about 3 atomic % of a first oxide former,

placing said core in said can;

inserting a CTE-reducing material selected from the group consisting of Nb, Ta, Ti, NbTi, NiAl, Ni<sub>3</sub>Al, V,  
20 Cr, Zr, Pd, Sb and mixtures thereof into said can;

co-reducing said can said core and said CTE-reducing material to form an article;

~~deforming said co-reduced article by mechanical~~  
techniques; and

25 heat treating said planar deformed alloy article to develop surface bi-axial texture.

55. The process of claim 54 further comprising the steps of:

rolling said alloy article; and

30 annealing said rolled alloy article without recrystallization to achieve a 5 to 50 nanometer Ra surface roughness.

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56. A product formed by the process of claim 54.

57. A process for forming a superconducting composite comprising the steps of forming substrate by:

- 5 preparing a can of copper, nickel, or copper-nickel and about 0 to about 3 atomic % of a first oxide former selected from the group consisting of Mg, Al, Ti, Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu, Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La, and mixtures thereof;
- 10 preparing a core comprising about 0 to about 100 atomic % of a second oxide former selected from the group consisting of Mg, Al, Ti, Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu, Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La, and mixtures
- 15 thereof, and about 0 to about 60 atomic % nickel, with the balance being copper;
- placing said core in said can;
- co-reducing said core and said can to form an
- 20 alloy article;
- planar deforming said alloy article;
- heat treating said planar deformed alloy article to develop surface biaxial texture; and
- coating said heat treated alloy article with a
- 25 superconducting oxide on at least one surface thereof.

58. An alloy article having biaxially textured surfaces comprising,

- about 0.1 to about 25 atomic % of an oxide former selected from the group consisting of Mg, Al, Ti,
- 30 Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu, Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La, and mixtures thereof;
- about 0 to about 60 atomic % nickel;

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with the balance being copper;  
said alloy article having a 5 to 50  
nanometers Ra surface roughness.

59. An alloy article having biaxially textured  
5 surfaces comprising,  
an alloy article and a rod of CTE-reducing  
material selected from the group consisting of Nb, Ta,  
Ti, NbTi, NiAl, Ni<sub>3</sub>Al, V, Cr, Zr, Pd, Sb and mixtures  
thereof within said substrate to control the co-efficient  
10 of thermal expansion of said substrate;  
said substrate comprising:  
about 0.1 to about 25 atomic % of an oxide  
former selected from the group consisting of Mg, Al, Ti,  
Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu,  
15 Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La, and mixtures thereof;  
and  
~~about 0 to about 60 atomic % nickel;~~  
with the balance being copper.
- 

60. An article, comprising an alloy that includes  
20 copper, nickel and at least about 1 atomic percent of a  
metal selected from the group consisting of Mg, Al, Ti,  
Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu,  
Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La and combinations  
thereof, wherein the article has a biaxially textured  
25 surface.
- 

61. The article according to claim 60, wherein  
the article is a superconductor substrate.

62. The article according to claim 60, wherein  
the alloy comprises at least about 2 atomic percent of  
30 the metal.

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63. The article according to claim 60, wherein the alloy comprises at most about 4 atomic percent of the metal.

64. The article according to claim 60, wherein the article has a cube textured surface.

65. The article according to claim 60, wherein the metal is aluminum.

66. The article according to claim 65, wherein the alloy comprises at least about 2 atomic percent aluminum.

67. The article according to claim 65, wherein the alloy comprises at most about 4 atomic percent aluminum.

68. The article according to claim 65, wherein the alloy comprises at least about 25 atomic percent nickel.

69. The article according to claim 60, wherein the alloy comprises at least about 25 atomic percent nickel.

70. The article according to claim 60, wherein the metal is aluminum and the alloy further includes at least one metal different from nickel, copper and aluminum.

71. An article, comprising an alloy that includes copper and nickel, the alloy having a native oxide exterior comprising alumina.

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72. The article according to claim 71, wherein the article comprises a superconductor substrate.

73. The article according to claim 71, wherein the alumina has a biaxially textured surface.

5 74. The article according to claim 71, wherein the alumina has a cube textured surface.

75. The article according to claim 71, wherein the alloy further comprises aluminum.

10 76. The article according to claim 71, wherein the alloy further includes aluminum and at least one additional metal selected from the group consisting of Mg, Ti, Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu, Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La and combinations thereof.

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15 77. An article, comprising an alloy of copper and at least about 25 atomic percent nickel, wherein the article has a biaxially textured surface.

78. The article according to claim 77, wherein the alloy comprises up to about 60 atomic percent nickel.

---

20 79. The article according to claim 77, wherein the biaxially textured surface is cube textured.

80. The article according to claim 77, wherein the article is a superconductor substrate.

25 81. The article according to claim 77, wherein the alloy further comprises at least about 1 atomic percent of a metal selected from the group consisting of

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Mg, Al, Ti, Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu, Th, Er, Tm, Be, Ce, Nd, Sm, Yb, La and combinations thereof.

82. The article according to claim 81, wherein  
5 the metal is aluminum.

83. The article according to claim 82, wherein the alloy further includes at least one metal different from copper, nickel and aluminum.

84. The article according to claim 77, wherein the  
10 article has a native oxide exterior comprising alumina.

---

---

100

101	SELECT AND WEIGH THE CONSTITUENTS Cu, E, AND OPTIONAL Ni.
102	MELT THE CONSTITUENTS.
103	(OPTION) REMELT TO ENHANCE HOMOGENEITY.
104	SHAPE THE SOLIDIFIED MELT AND HOMOGENIZE BY HEAT TREATMENT.
105	DEFORM THE SHAPE TO A SMALLER SIZE AND RECRYSTALLIZE TO FORM A SMALL GRAIN SIZE IF DESIRED.
106	DEFORM THE SHAPE IN AN AXIALLY SYMMETRIC MANNER TO A SMALLER SIZE.
107	DEFORM THE ALLOY IN A PLANAR MANNER TO A REDUCTION IN THICKNESS EXCEEDING 85% BUT NOT MORE THAN 99.9%
108	HEAT TREAT AT A TEMPERATURE EXCEEDING 250°C BUT NOT MORE THAN 95% OF THE MELTING TEMPERATURE.
109	(OPTION) ANNEAL IN A GAS FLOW WITH LOW OXYGEN, PARTIAL PRESSURE TO FORM AN EPITAXIAL OXIDE LAYER.

FIG. 1

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200

201	PREPARING A CAN USING Cu, CuNi OR Ni STOCK, OR Cu, CuNi OR Ni ALLOYED WITH A SMALL AMOUNT OF OXIDE FORMER (< 1-3 AT %).
202	PREPARING Cu, Ni, OR CuNi CORE ALLOYED WITH 0 TO 100 ATOMIC % OXIDE FORMER.
203	PLACING CORE 302 IN CAN 301 AND CO-REDUCING THE COMPOSITE ASSEMBLY TO A SMALLER CROSS SECTION.
204	DEFORMING TO THE STARTING SIZE FOR THE PLANAR ROLLING TO COMMENCE.
205	PLANAR DEFORMING THE COMPOSITE TO A REDUCTION IN THICKNESS BETWEEN 85%-99.9%.
206	HEAT TREATING TO DEVELOP A CUBE TEXTURE IN THE SHEATH, AND INDUCE HOMOGENIZATION IN THE SUBSTRATE.
207	(OPTIONAL) ANNEAL IN A GAS FLOW WITH A LOW OXYGEN PARTIAL PRESSURE TO FORM AN EPITAXIAL OXIDE LAYER.

FIG. 2

300

301	PREPARING A CAN USING Cu, CuNi OR Ni STOCK, OR Cu, CuNi OR Ni ALLOYED WITH A SMALL AMOUNT OF OXIDE FORMER (< 1-3 AT %).
302	SELECT AND WEIGH THE CONSTITUENT METAL OR ALLOY POWDERS AND PLACE IN THE CAN.

FIG. 3



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400	SELECTING Ni, CuNi, OR Cu POWDER OR FOILS, THAT CONTAIN 0.2 TO 1 WEIGHT % OXYGEN.
401	SELECTING ADDITIONAL POWDERS OR FOILS FOR A TOTAL CONCENTRATION, WITH 401, OF 3 TO 50 AT % OXIDE FORMER, 0 TO 60 AT % Ni, BALANCE COPPER.
402	FILLING A CAN AND PROCESSING THE POWDER MIXTURE ACCORDING TO 203-205. NO ANNEALS ARE APPLIED UNTIL THE FINAL TEXTURING HEAT TREATMENT.
403	HEAT TREATING ACCORDING TO 206 AND (OPTION) 207 SO THAT A SMALL AMOUNT OF THE OXIDE FORMER ABSORBS THE OXYGEN IN THE Ni, CuNi, OR CU POWDERS AND FORMS OXIDE PARTICLES, WHICH STRENGTHEN THE SUBSTRATE.

FIG. 4

500	SELECTING ANY OF THE FOUR PROCESSES 100-400 OR PRIOR ART SUBSTRATE-FORMING PROCESSES TO MAKE A SUBSTRATE WITH REDUCED CTE.
501	PLACING A ROD OF CTE-REDUCING MATERIAL IN THE BILLET OR CORE.
502	PROCESSING THE BILLET OR CORE ACCORDING TO 100-400, INTO THE FINAL SUBSTRATE TO PRODUCE A FINAL SUBSTRATE WITH A LOW CTE CORE WHICH REDUCES THE OVERALL CTE OF THE SUBSTRATE.

FIG. 5

600

601	SELECTING ANY OF THE FIVE PROCESSES 100-500 OR PRIOR ART SUBSTRATE-FORMING PROCESSES TO MAKE A SUBSTRATE WITH REDUCED SURFACE GROOVING AND COMPLETING ANY OF THE FIVE PROCESSES INCLUDING THE TEXTURING ANNEAL.
602	ROLLING THE SUBSTRATE.
603	LOW TEMPERATURE STRESS ANNEALING THE SUBSTRATE IN A PROTECTIVE ATMOSPHERE WITHOUT RECRYSTALLIZATION TO PRODUCE A SUBSTRATE HAVING A SMOOTH SURFACE.

FIG. 6

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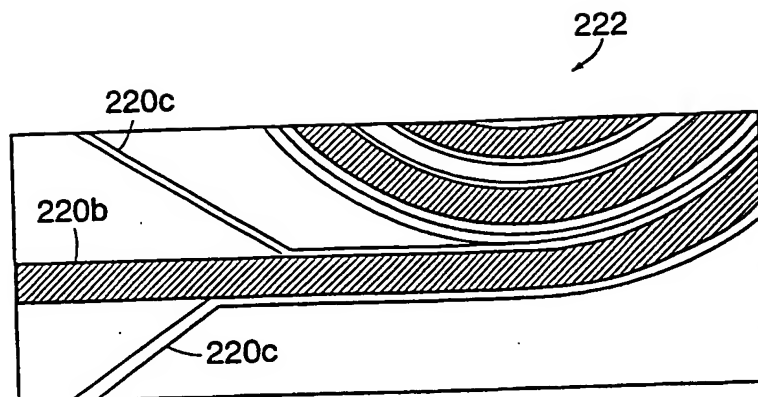


FIG. 2A

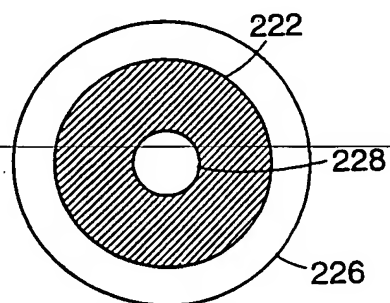


FIG. 2B

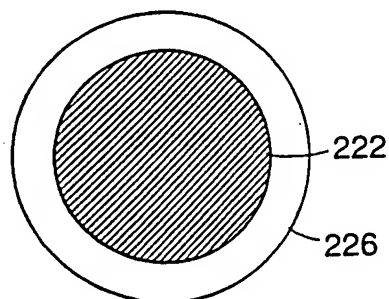


FIG. 2C

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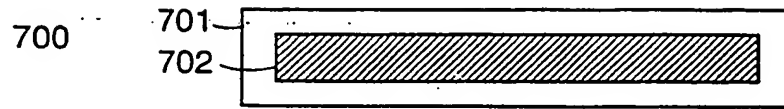


FIG. 7



FIG. 8

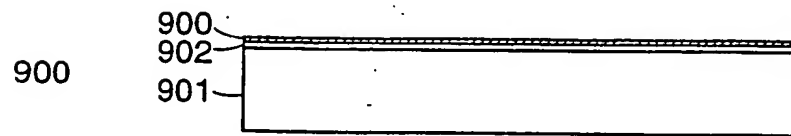


FIG. 9

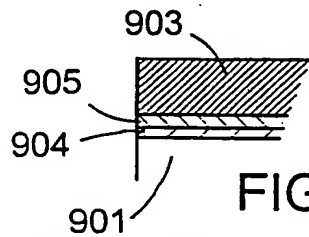


FIG. 9A

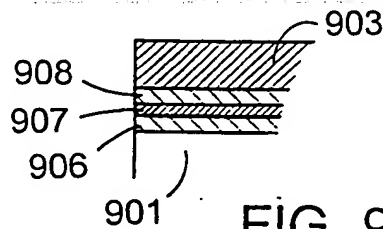


FIG. 9B

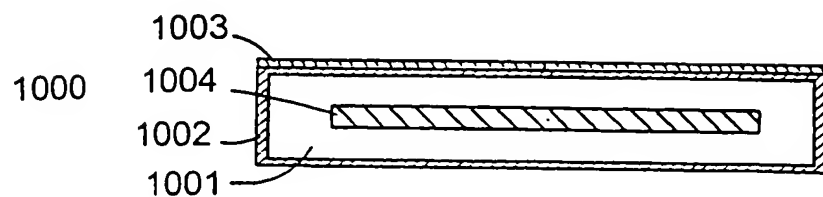


FIG. 10

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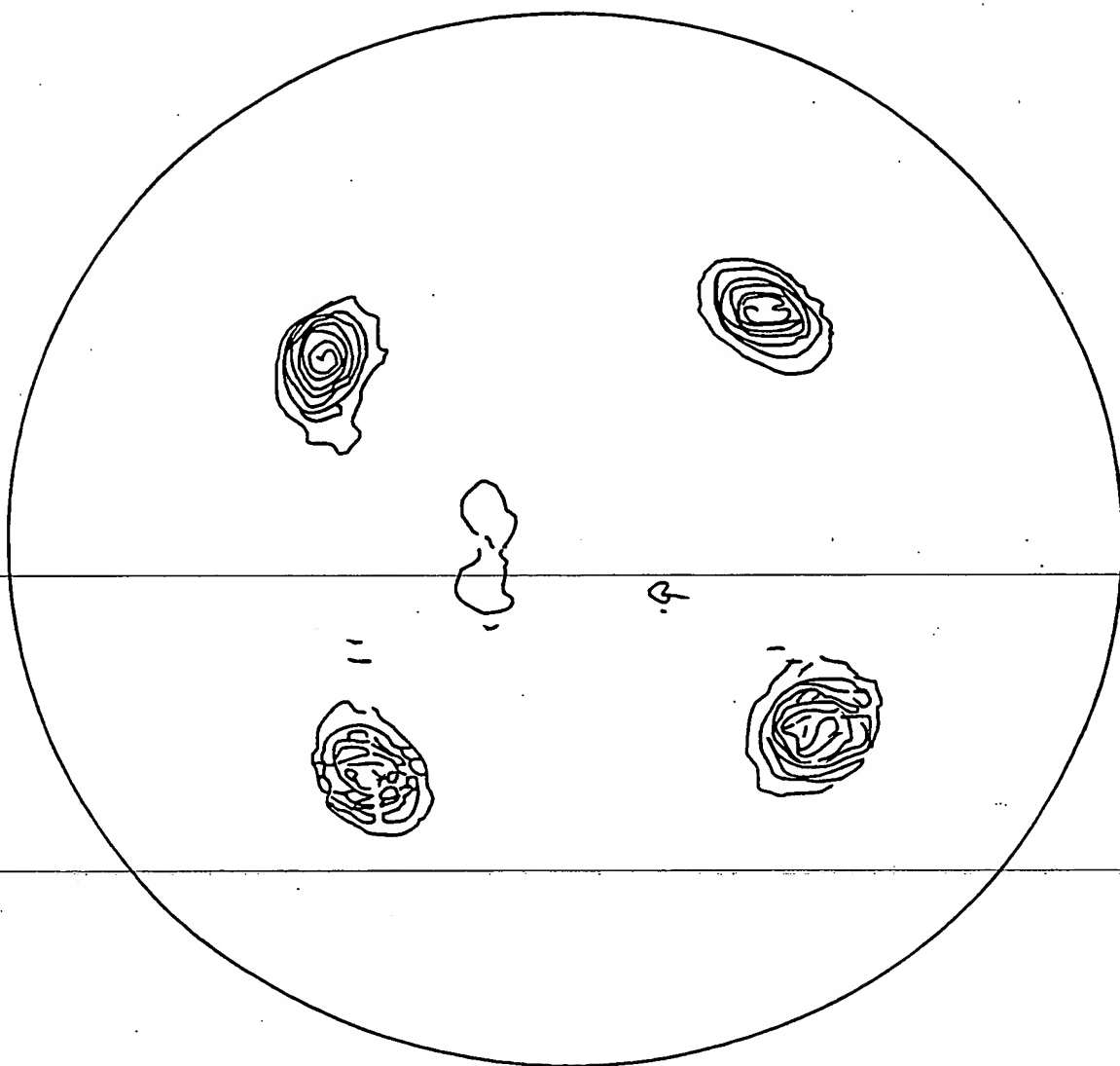


FIG. 11

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/20404

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :Please See Extra Sheet

US CL :Please See Extra Sheet

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 505/230, 236, 237, 238, 239, 470, 813, 826; 419/19, 29, 43; 420/457, 485, 489, 490, 492, 494, 495; 252/512; 72/199

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, CAS (search terms include: biaxial? text?; alloy; superconduct?; cubic)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GOLDACKER ET AL Biaxially textured substrate tapes of Cu, Ni, alloyed Ni, (Ag) for YBCO films, Applied Superconductivity 1997, Vol 2, pp 1279-1282, see Abstract.	1-20, 40-49, 58-84
Y	US 5,164,360 A (WOOLF et al) 17 November 1992 (17-11-92), see Abstract; Col 2, lines 57-61; Col 4, lines 1-8 and lines 48-51.	1-20, 40-49, 58-84
Y	US 5,047,389 A (WOOLF et al) 10 September 1991 (10-09-91), see Abstract; Col 2, lines 45-66; Col 4, lines 43-48.	1-20, 40-49, 58-84
X,P	US 5,739,086 A (GOYAL et al) 14 April 1998 (14-04-98), see Abstract; Col 4, lines 9-19; Col 9, lines 17-27 and lines 49-56.	1-20, 40-49, 58-84

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

10 MARCH 1999

Date of mailing of the international search report

18 MAR 1999

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
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Telephone No. (703) 308-0661

International application No.  
PCT/US98/20404

International application No.  
PCT/US98/20404

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 5,063,200 A (OKADA et al) 05 November 1991 (05-11-91), see Abstract; Col 3, lines 6-27; Col 4, ines 19-23 and lines 50-55.	1-20, 40-49, 58-84
X --- Y	US 5,089,057 A (PLEWES) 18 February 1992 (18-02-92), see Abstract; Col 3, lines 25-31; Col 7, lines 1-23 and lines 52-68; claims.	1-2, 13-20, 58-84 --- 3-12, 40-49
A	US 4,640,816 A (ATZMON et al) 03 February 1987 (03-02-87), see Abstract; examples.	1-84
A	US 3,982,973 A (PETERS et al) 28 September 1976 (28-09-76), see Abstract; claims.	1-84

**INTERNATIONAL SEARCH REPORT**

International application No.  
PCT/US98/20404

**A. CLASSIFICATION OF SUBJECT MATTER:**  
IPC (6):

H01B 12/02; B32B 15/04, 18/00; C22C 9/00, 9/06, 19/03; C04B 35/622; B22F 1/00, 3/18, 7/02

**A. CLASSIFICATION OF SUBJECT MATTER:**  
US CL :

505/230, 236, 237, 238, 239, 470, 813, 826; 419/19, 29, 43; 420/457, 485, 489, 490, 492, 494, 495; 252/512; 72/199